

# Phase Transition of the Normal Metallic State to the Antiferromagnetic Spin Density Wave State in (TMTSF)<sub>2</sub>PF<sub>6</sub>

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Phase Transition of the Normal Metallic State to the  
Antiferromagnetic Spin Density Wave State in  $(\text{TMTSF})_2\text{PF}_6$

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## Abstract:

A helium gas -pressure system has been tested and then used to investigate the nature of a phase transition from the normal metallic state to an antiferromagnetic spin density wave state in the quasi -one dimensional molecular organic conductor  $(\text{TMTSF})_2\text{PF}_6$ . This metallic state superconducts at low temperature and high pressure, in such a way that the insulating antiferromagnetic state competes with the superconducting state. The physics motivation was to examine the possibility of a “quantum critical point” near the critical pressure of the sample where these latter two states may coexist. The technical motivation was to make the first tests of the pressure system at cryogenic temperatures to ensure that it is the appropriate tool for the planned investigations. Using temperature sweeps at various fixed pressures on a single crystal sample, we were able to obtain several points on the pressure versus temperature phase boundary separating the metallic and SDW states. We have thus verified that the helium gas-pressure system is indeed capable of facilitating these types of experiments, and future measurements will be done at lower temperatures accessing the superconducting state.

## Introduction/Background:

$(\text{TMTSF})_2\text{PF}_6$ , a highly anisotropic, quasi -one dimensional, molecular organic conductor, has been studied extensively over the past twenty years. At low temperatures and high pressures, the metallic state superconducts. It can also be an insulator at low temperatures and low pressures. Up until the last few years, scientists have thought that the transition took place in such a manner that the sample would switch from one state to another sharply and clearly, meaning that the sample would never be in two states at once over a detectable temperature range.

But with better and more precise equipment, that concept has been challenged by new data that shows a definite coexistence of the metallic and spin density wave (SDW)

states and indicates that there is also a coexistence between the SDW and superconducting states.

It is currently thought that the phases in  $(\text{TMTSF})_2\text{PF}_6$  and other similar superconductors, compete with one another near the critical pressure and critical temperature to form a realm where two states coexist to varying degrees. At most points of the transitions, in the pressure-temperature plane, between either the metallic to the SDW state or the superconductor to the metallic state, there is a clear line that separates each individual phase that is consistent with older theories and experiments, but very near the critical points, that transition becomes hazy and the two states for both cases appear to overlap. It is well known that there is an area in the phase diagram where the metallic and SDW states coexist, from experiments using a type of pressure generation different from what is used in the present work.

Figure 1[1]

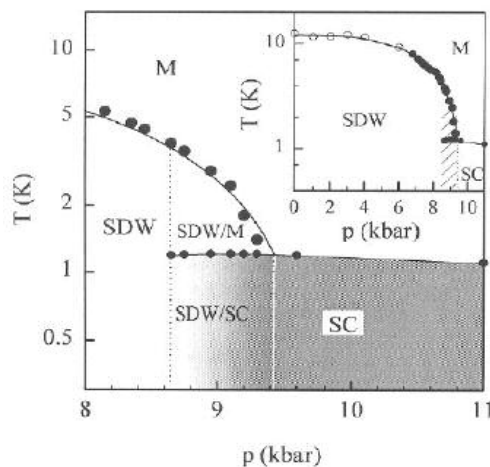
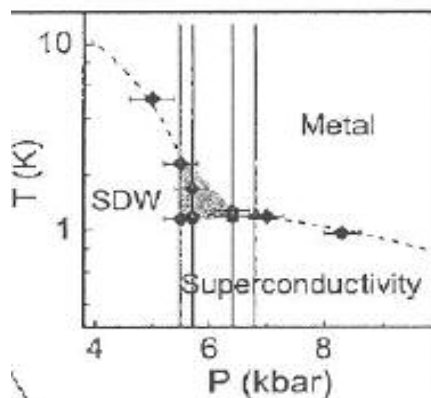


Figure 2[2]



This phenomenon occurs at pressures that are lower than the critical pressure, but still near it. Since  $(\text{TMTSF})_2\text{PF}_6$  is a layered material of alternating metallic/superconducting and insulating layers, one can infer that the coexistence of the two states could be due to having one layer superconducts and another layer be an insulator, but this thought has been discounted due to experiments showing otherwise. [3] It is likely due to the fact that the insulating (SDW) gap is not opened at all points of the Fermi Surface, so small pockets of unpaired charge carriers exist.

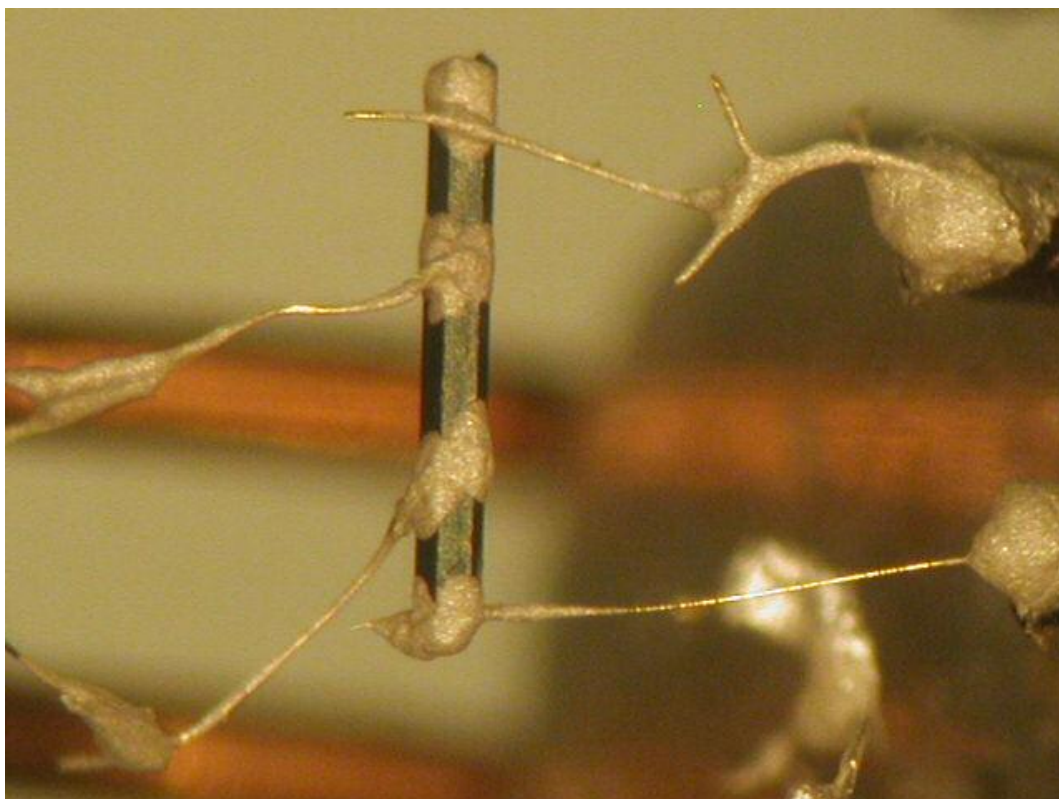
The greater question is what is the nature of the phase transition between the superconducting and SDW states. It is a gray area where scientists have been unsure of whether or not there is a clean transition or not. Recently there has been evidence that there is a coexistence between the two states that is similar to the metallic/SDW state. It could be due to a “quantum critical point” (QCP), or a first order transition line between the two states. On the other hand, this haziness could be simply due to inhomogeneous pressure (non-hydrostatic), such that different parts of the sample are in different conducting states.

A critical point is a point in the phase diagram of a material where two or more states are very close to each other. In the case of  $\text{H}_2\text{O}$ , there is a critical point at a critical temperature ( $T_c$ ) where the  $\text{H}_2\text{O}$  changes from a solid to a liquid, there are also other critical points where it changes states again. At this point there is a coexistence between the water state and the ice state. Some of the molecules are liquid and some are solid, but there is a dynamic equilibrium between the two states where the molecules are constantly changing states, but the material as a whole appears the same. This *dynamic equilibrium* is due to thermal fluctuations in the material. Tiny changes in the temperature drive the sample to change states from ice to water and back again. As one moves farther away from the critical point, one state dominates until the entire sample is in one state far enough away from the critical point.

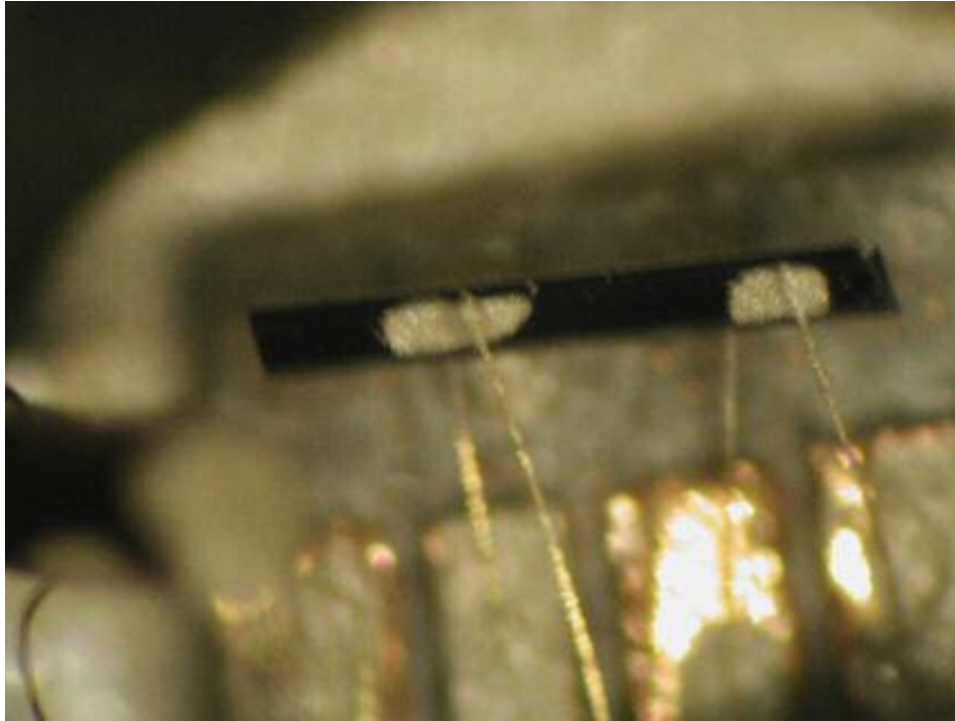
A “quantum critical point” is one where the temperature is at 0 K, or absolute zero and there can thus be no thermal fluctuations. There are only quantum fluctuations. Zero point energy leads to quantum fluctuations, which then play the role of thermal fluctuations and drive a phase transition.

## ExperimentalDetails:

Over the Fall 2002 and Spring 2003 semesters, we have run tests on two single crystal  $(\text{TMTSF})_2\text{PF}_6$  samples.



**Sample1** Figure3



**Sample2** Figure4

Electrical connections were made using 12um diameter gold wires attached by silver paint for a 4-probe setup. The sample, along with a 1030-Cernox thermometer, a Type T (constantan-copper) thermocouple (more information on the thermocouple in the appendix) and a pressure gauge made of a single crystal of heavily doped n-InSb were placed inside a small beryllium-copper gas pressure cell. (diagrams of the pressure cell and the VTI system in the appendix)

See figures of pressure cell below

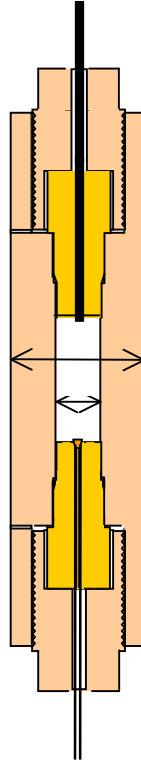
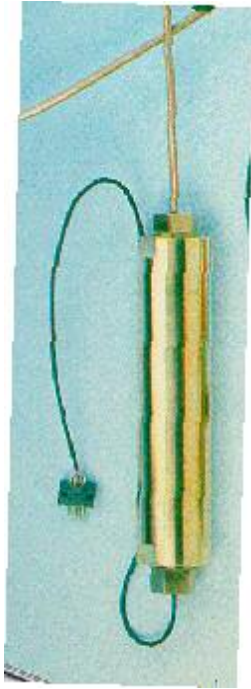


Figure5Figure6

The cell is attached, through long stainless steel and BeCu capillary tubes, to the gas compressor U11 that can reach up to 15kbar.

Figure7





There is another Type T thermocouple on the shaft of the probe to measure the temperature after the helium gas has passed the cell. One benefit of the gas-pressure system is that we are able to make small changes in the pressure without having to remove the sample from the pressure cell. Another is that this means of generating pressure yields much better homogeneity of pressure (hydrostatic) compared to all other techniques, a useful fact in testing whether the observed phase-state mixing in  $(\text{TMTSF})_2\text{PF}_6$  is intrinsic or not.

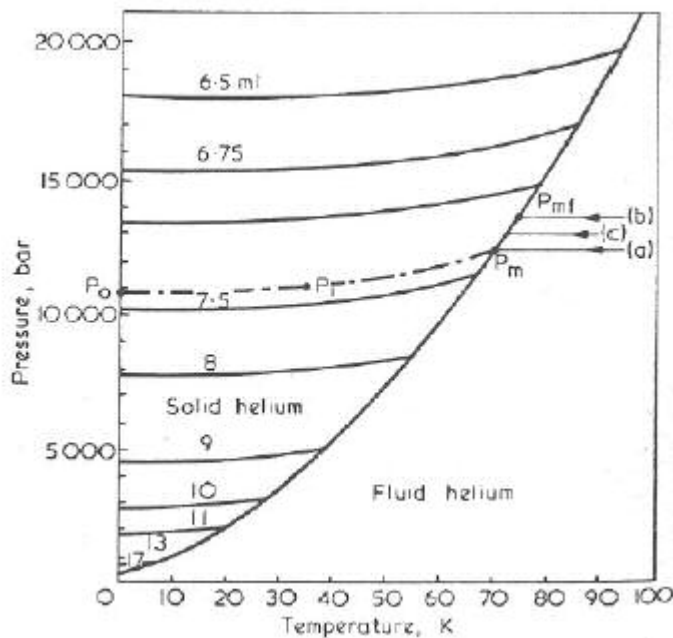
A Stanford Research Systems model SR830 lock-in-amplifier was used to apply low frequency current to the sample, while also measuring the resistance of the sample. Another SR830 was used to monitor the resistance of a pressure sensor inside the BeCu cell. A PAR5209 lock-in-amplifier was used for the Cernox thermometer, a HP3478A for the internal thermocouple, a K181 nanovoltmeter for the outside thermocouple, a K182 for the pressure in the capillary outside of the cell, and a Lake Shore 93C-1 temperature controller to control and measure the temperature of the vaporizer (calibration numbers for the vaporizer heater in the appendix). A K224 digital current source was later added as a current source for the vaporizer heater instead of the Lake Shore one since our software could use the K224 for a controlled temperature sweep by stepping the current output. We later switched the internal TC to a K182, the external TC to a HP3478A and the external pressure gauge to a K181 for increased sensitivity in the measurements of the internal TC.

We suspect that the first sample had its wires arranged in a  $R_{xx}$  setup since the  $4\text{-}\Omega$  probe resistance at room temperature on the bench was  $3.4\text{ ohms}$ , while we had intended to measure the higher resistance  $R_{zz}$  direction for a better signal-to-noise ratio. Temperature sweeps were done at a pressure of  $0.56\text{ kbar}$ , but before we could raise the pressure to another level and do more tests, the sample broke. The second sample is in a  $R_{zz}$  setup according to our  $4\text{-}\Omega$ -probe resistance value of  $233\text{ ohms}$ . On this sample, we were able to record temperature sweeps at pressures of  $0.55\text{ kbar}$ ,  $2.64\text{ kbar}$ , and  $4.7\text{--}4.4\text{ kbar}$ .

Temperature sweeps were achieved in three ways. One was a “natural” cooling in the VTI after removing the heat from the VTI vaporizer heater or the local heater on

the pressure cell. A second was a “natural” warming enabled by closing the VT needle valve, thus removing the source of the cooling power. The third method was to step the current output from a K224 current source. For each temperature sweep, we would hold the pressure constant and then record the data using a LabView software program. In order to change the pressure, we would hold the temperature constant and then raise the pressure. When changing the pressure, we would need to raise the temperature of the sample as specific amounts so that the liquid helium in the cryostat wouldn’t solidify under the higher pressures.

Figure 8 [4]



There are three separate stages to our gas-pressure system. Stage 1 is in the pressure range of 0 to 0.7 kbar. Stage 2 is from 0.7 to 3.5 kbar and Stage 3 is from 3.5 to 12 kbar. We could only go to one pressure per stage while raising the pressure, but once we reached a certain pressure, we could make as many changes as we wanted when lowering the pressure. Only in raising it were we confined to three pressures.

## Data Analysis:

There are two main sets of data that we took: pressure changes and temperature sweeps.

As in any experiment, we ran into a few problems ranging from equipment malfunctions to having a sample break in half in the middle of a run. The first set of temperature sweep data includes all good and all bad runs that we had. We then took out the ones that had problems so that the second set of data is all good as far as we can infer at this time. The biggest problem that we ran into was trying to keep the thermocouples at a constant reference temperature. The ice would continuously melt over time and that change in the reference temperature wreaked havoc on our data until we put the thermocouples into a large chunk of copper to create a large thermal mass. We then stuck this entire block of metal into the ice. From this point on the thermocouples were much more stable and reliable. So because of this problem we were forced to rule out any data where the thermocouple was not at 0 degrees Celsius. There were also a few runs where the needle valve would freeze, causing us to warm up the entire VTI in an attempt to unblock it. But far and away the worst and most persistent problem that we encountered was the one of achieving a thermal equilibrium within the pressure cell. There was a huge time constant associated with this equilibrium and we are not certain that any of the runs achieved an acceptable thermal equilibrium. Those three problems were the most prevalent. There were a few other problems such as software malfunctions, but most of those problems were small and easily fixed and thus did not interfere with the data.

After analyzing all of the data, we decided that there were three runs (040203t8.dat, 040303prla.dat, 040903t4.dat) where we felt there conceivably was good thermal equilibrium in the pressure cell and the data of the measurements of the sample were the most reliable and accurate that we have. These runs were then plotted together to show how the critical temperature of the sample changes over a range of pressures.

Graphs 1 -4 are resistance versus temperature measurements from various instruments on the first sample at 0.64 kbar. Graphs 14 -18 are also of the first sample and they are set up in the same manner. In both sets we are unsure as to whether or not

there was any thermal equilibrium inside the pressure cell and that is why we will not compare this data to what other scientists have seen in previous experiments. The second set of graphs had no real discernable problem except for the thermal equilibrium one. So all data that is on the first set of graphs but not on the second set had serious problems, most of which turned out to be instrumental malfunctions.

All temperature measurements with the cernox thermometer were inconsistent with itself, meaning that the data did not come out in a clean manner. When looking at the graphs of the VTI temperature, one must keep in mind that the VTI thermometer is outside the pressure cell and would reach thermal equilibrium much quicker than anything inside the cell, so all of the data shows the transition between the states occurring at 4 K when the temperature of the sample was much higher than that when the VTI reached 4.2 K. The only thermometer that we had any faith in was the internal thermocouple. But again it was located far enough away from the sample that there was a thermal gradient inside the cell that threw off some of the data. Even still we believe that the three runs (040203t8.dat, 040303prla.dat, 040903t4.dat) may have reached thermal equilibrium, so we took the voltage measurements from the internal thermocouple and tried to calculate what the temperature of the inside of the cell was from that. The T calc measurements are the results that we get and it seems to work somewhat well in the range of the transition temperature.

Graphs 5 -7 and 19 -22 are resistance versus temperature measurements of the second sample at 0.55 kbar. Again there was a huge problem with thermal equilibrium and the inconsistent thermocouple reference temperature, so we were forced to disregard most of the data and focus on run 040203t8.dat as the one run that may have achieved thermal equilibrium.

Graphs 8 -10 and 23 -26 are temperature sweeps of the second sample at 2.64 kbar. There were similar problems at this temperature, so we focused on run 040303prla.dat.

Graphs 11 -13 and 27 -30 are temperature sweeps of the second sample at a range of 4.7 to 4.0 kbar. The run we focused on here was 040903t4.dat.

Graphs 31 -33 are of the pressure change from .15 to .64 kbar on the first sample at 293 K. The attempt to calculate the internal pressure by using the resistance measurements from the internal pressure gauge were not as successful as could have been

hoped. There is also a graph of temperature, sample resistance, and pressure using various instruments versus time and versus the resistance of the internal pressure gauge.

Graphs 34 -36 are of the pressure change from .15 to .55 kbar on the second sample at a temperature of 293K.

Graphs 37 -39 are of the pressure change from .55 to 2.64 kbar on the second sample at a temperature of 60K.

Graphs 40 -41 are of the pressure change from 2.64 to 7.0 kbar on the second sample at a temperature of 75K.

Graphs 42 -45 are of the leakage that occurred over time ranging from 6.25 to 4.4 kbar on the second sample. The leakage occurred until it reached an equilibrium level of around 4.4 kbar for most of the runs. The pressure did go down to about 4.0 kbar by the final run.

Graphs 46 -47 are of the decrease in pressure from 4.0 to 0.15 kbar on the second sample at a temperature of around 86K.

Graphs 48 and 49 are comparisons of the different resistance versus temperature plots on the T<sub>calc</sub> scale of the three runs at different pressures that were quasi-reliable. It is easy to see that as the pressure increased, the transition temperature dropped which is consistent with previous experiments.

Graph 50 is a phase diagram of the sample. Our data is the dots and the lines are rough results of what other scientists have seen in previous experiments.

Data

TemperatureSweepsat0.64kbar

TemperatureSweepsat0.55kbar



TemperatureSweepsat2.64kbar

TemperatureSweepsat4.4kbar

PressureChangefrom0.15to0.64kbarat293K

PressureChangefrom0.15to0.55kbarat293K

PressureChangefrom0.55to2.64kbarat60K

PressureChangefrom2.64to7.0kbarat75K

## ComparisonGraphs

## Conclusion:

From the detailed section of the comparison graph that shows the resistance of the sample versus temperature at three pressures, it can be derived that the transition temperature at the three pressures is as follows:

| Pressure(kbar) | Temperature(K) |
|----------------|----------------|
| 0.55           | 11.7+/- 0.2    |
| 2.64           | 9.8+/- 0.2     |
| 4.43           | 8.8+/- 0.2     |

When I take this data and put it into a pressure -temperature phase diagram and compare that to what other scientists have found, the two sets of data are very similar, indicating that the gas-pressure system is certainly capable of the types of measurements that we will need to look at the SDW/superconducting region in later experiments.

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## Appendix: